

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

USING TRIMETHYLSILANE TO IMPROVE SAFETY, THROUGHPUT AND VERSATILITY IN PECVD PROCESSES

M.J. Loboda, J.A. Seifferly, C.M. Grove and R.F. Schneider
Dow Corning Corporation, Midland, MI 48686

ABSTRACT

Despite an extensive amount of experience in the handling and use of SiH_4 , the semiconductor manufacturing community still has safety concerns regarding future applications of this material. The issues are related to the increasing volume requirements in device manufacturing. As this requirement forces higher operating efficiency, equipment shut down time for repair or maintenance becomes more expensive. Trimethylsilane ($(\text{CH}_3)_3\text{SiH}$) is a non-pyrophoric organosilicon gas which can be used as a safe replacement for silane. Its material properties allow for standard packaging and quick integration into plasma deposition processes for common dielectric films with potential for reduced cost of ownership. The use of a non-pyrophoric gas will increase safety and process equipment uptime. By direct comparison to silane based processes, it is demonstrated that comparable quality films of silicon dioxide and silicon nitride can be deposited from trimethylsilane. In addition, inert amorphous silicon carbide films can be deposited using the gas as a single precursor. The precursor properties and process characteristics are compatible with the increasing demands of semiconductor manufacturers.

INTRODUCTION

Plasma enhanced chemical vapor deposition (PECVD) processes are used extensively in the fabrication of semiconductor integrated circuits. For example, dielectric interlayers and passivation layers are formed using PECVD processes for silicon dioxide and silicon nitride. Silane (SiH_4), a pyrophoric gas, is the traditional source for silicon in PECVD processes. As manufacturing demands force capacity requirements to increase, IC manufacturers are confronted with new challenges with regards to transportation, storage and delivery of silane. While considerable application experience has helped to minimize the risks associated with handling such a dangerous material, accidents associated with gas discharge still occur. Small leaks are also an issue with SiH_4 , resulting in uncontrolled formation of oxide powders in the gas plumbing and pumping systems, producing costly down time for cleaning and/or repair. Finally, higher volume manufacturing requires larger amounts of SiH_4 be stored on location, creating a growing explosion hazard.

Because of these issues, there continues to be interest in new silicon source materials for PECVD applications. A new silicon source material should offer improved safety, be applicable to a wide range of thin film processes and not increase cost of ownership. Organosilicon materials, such as TEOS (tetraethoxysilane) and diethylsilane, are commercially available precursors which can be used in place of silane. While these materials offer improved safety, their comparatively low vapor pressure requires the use of specialized delivery systems to accurately meter the precursor to the deposition chamber.

This increases both capital and maintenance costs by adding more equipment to the fabrication area. Currently, the volume of applications using TEOS for the deposition of oxide films continues to increase, yet the IC manufacturing community has not embraced a safe alternative to silane which it could easily adopt across the full spectrum of dielectric film processes used in device fabrication.

Trimethylsilane ((CH₃)₃SiH) is a non-pyrophoric organosilicon gas which can be used as a substitute for SiH₄. The physical properties of trimethylsilane are shown in Table 1. The room temperature vapor pressure of trimethylsilane affords full compatibility with packaging and delivery techniques currently used for silane. In contrast, the non-pyrophoric character of trimethylsilane offers the ability to reduce the danger associated with cylinder changeover and large volume storage.

Table 1. Physical properties of trimethylsilane.

Molecular Formula:	H ₁₀ C ₃ Si
Molecular Weight:	74.19 g/mol
Vapor Pressure:	1400 torr @25° C
Approximate Gas Density:	3 mg/cm ³
D.O.T Specification:	UN3161 Liquefied Gas, Flammable
Mass Flow Coefficient:	0.27 (relative to N ₂)
Impurities (ppm by volume):	Air <1.0 ppm Hydrocarbons <5.0 ppm Carbon dioxide <1.0 ppm Water <1.0 ppm Metals: Nondetectable by ICP-MS

In process tools operating at low pressures, the explosiveness and flammability of silane in the presence of oxidants is not known. Instances of silane accidents during processing make up greater than 24% of those recently reported in a SEMATECH survey [1]. Analysis often shows that the cause of most accidents involving silane can be traced to human error, and not mechanical failure [2]. The implementation of a non-pyrophoric Si source gas would have a positive impact on safety, reducing opportunities for human error. It can also help improve reliability. Probably not included in these reports are the more common occurrences of equipment failures or unscheduled maintenance/repair due to particle contamination. Such particle contamination, which results from the oxidation of silane in small volumes or condensation of pyrophoric reaction products in the effluent gas stream, can lead to wear or failure of pumping systems and mass flow controllers. Trimethylsilane does not readily oxidize in the presence of air or water vapor and will not form oxide dust in the presence of air leaks thereby helping extend system operation. Unlike SiH₄, trimethylsilane liquefies at cylinder pressures. This property allows larger quantities of trimethylsilane to be stored per package, minimizing the need for cylinder changes and the safety hazards associated with a pyrophoric gas.

EXPERIMENTS

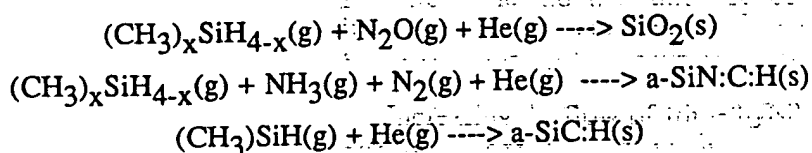
PECVD processes were conducted in a PECVD system of the type used for growth of silicon oxides and nitrides [3]. This system includes an *in-situ* residual gas analyzer for analysis of the reactant gas stream. The trimethylsilane source gas (Dow Corning™ 9-5170) was supplied to the system from a carbon steel gas cylinder fitted with a CGA-350 fitting, similar to silane. The cylinder was plumbed directly into the mass flow controller inlet. Trimethylsilane has an approximate flow coefficient of 0.27 relative to N₂.

Thin films of silicon dioxide and silicon nitride (a-SiN:H) were grown using either silane (10% SiH₄ in He) or trimethylsilane as the silicon source gas. Thin films of silicon carbide were also grown using only trimethylsilane as the precursor gas. In all PECVD experiments the RF power density, pressure, and total gas flow used were chosen to be comparable to that used in IC manufacturing. All films were deposited onto bare Si <100> substrates. Once deposited, the films were characterized using reflection-absorption Fourier transform infrared spectroscopy (RAS-FTIR), X-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), wafer curvature based film stress and stress versus temperature measurements, wet chemical etching and metal insulator semiconductor (MIS) capacitors.

PECVD Process Reactions

Electron impact (EI) ionization of trimethylsilane occurs in the plasma generating three Si-fragments of comparable abundance. This is shown in Figure 1, which is the mass spectrum for trimethylsilane recorded with a residual gas analyzer. The relative intensities of the primary fragments are consistent with the bond dissociation energies reported for trimethylsilane [4]. The dissociation energy associated with the loss of a Si-H bond is the same for both SiH₄ and trimethylsilane (about 3.9 eV) and is slightly more than that associated with the loss of a methyl group (3.8 eV). The major difference in the (EI) dissociation of trimethylsilane and SiH₄ is that very little SiH_x fragments are generated from trimethylsilane. Trimethylsilane's H-Si-CH fragments have a higher gas viscosity, thus lowering the flux of depositing species at the substrate. This implies slightly slower growth rates compared to SiH₄ should be expected under equivalent conditions [5].

The chemical reactions associated with plasma assisted growth of silicon oxide, silicon nitride and silicon carbide, are respectively :



where x=0 for SiH₄ or x=3 for trimethylsilane. The reaction products associated with the trimethylsilane based processes were characterized by residual gas analysis and are listed in Table 2. From analysis of the partial pressure data, we estimate that the reaction products represent 10-20% of the composition of the effluent gas stream.

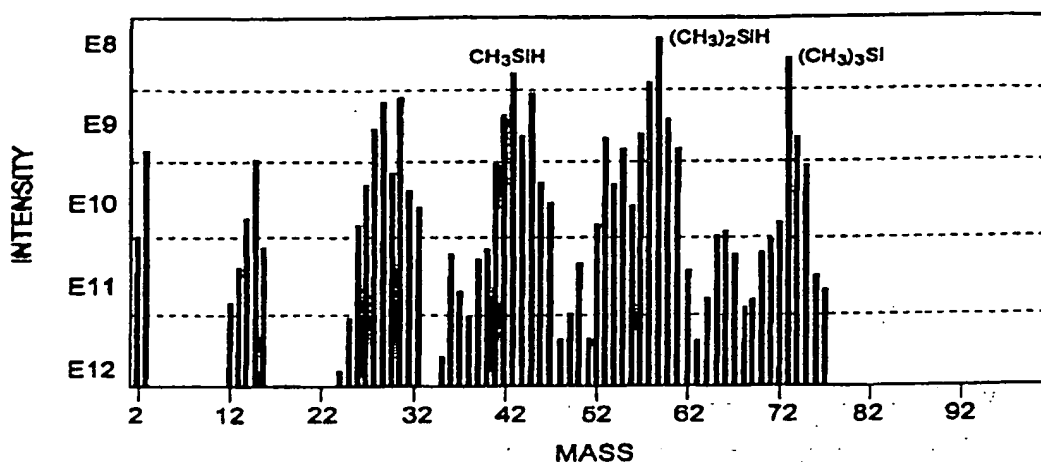


Figure 1. Mass spectrum of pure trimethylsilane with primary radical species identified.

Table 2. Reaction products identified in the effluent gas stream for PECVD processes using trimethylsilane.

<u>Silicon Oxide</u>	<u>Silicon Nitride</u>	<u>Silicon Carbide</u>
H ₂	H ₂	H ₂
N ₂	N ₂	CH ₄
C ₂ H ₆	C ₂ H ₆	C ₂ H ₆
NO ₂	C ₂ H ₂	C ₂ H ₄

Table 3 compares the deposition conditions and properties of oxide films grown at 375° C. These deposition conditions were adjusted to eliminate all hydrogen from the film and to produce equivalent growth rates for both processes (nominally 350 Å/min). Identical infrared spectra were obtained with both Si sources. Hydrogen bonds could not be observed in the IR spectra. RBS and XPS measurements confirmed that the films were stoichiometric and that this use of the trimethylsilane did not result in any carbon incorporation in the oxide film. Stress hysteresis was not observed in any of the films in stress versus temperature measurements up to 475° C in a N₂ ambient.

Increasing the flow of trimethylsilane from 6 to 12 sccm with 1235 sccm of N₂O and 125 sccm of He increased in the growth rate to about 1200 Å/min, but less than the silane process (1600 Å/min). An interesting property of the trimethylsilane-based oxide process is that the stress is consistently lower than the corresponding SiH₄ process, with tensile and compressive values in the range of ±100 MPa, whereas the SiH₄ based processes were in the consistently compressive at 200-300 MPa. At growth rates of 1200 Å/min and higher, Si-OH and H₂O bonds were observed in the IR spectra of the oxide films. The trimethylsilane process showed the higher H₂O levels, and as the trimethylsilane flow was

Table 3 - Example comparison of PECVD Oxide Films Grown at 375° C

	SiH ₄	(CH ₃) ₃ SiH
SiH ₄ Flow (sccm)	3	0
(CH ₃) ₃ SiH Flow (sccm)	0	6
N ₂ O Flow (sccm)	375	475
He Flow (sccm)	152	475
Pressure (torr)	1.9	1.9
Power (W)	25	100
Compressive Film Stress (MPa)	270	100
Wet Etch Rate (10:1 BOE)(Å/s)	45	43
Relative Dielectric Constant	3.82	3.83
Dielectric Breakdown Strength (MV/cm)	7-8	7-8

increased to 24 sccm, the film stress became tensile, the H₂O bond density dropped and C-H bonds could be observed. Presuming this indicates that H_xC_y-SiH species are absorbed on the wafer, two reaction pathways can produce oxide formation. These are the oxidation of the Si-H and Si-CH₃ bonds. The Si-CH₃ bond is harder to oxidize. When it is cleaved from the surface the hydrocarbon fragment provides an additional source of hydrogen in the plasma. The hydrogen can react with oxygen to form water which may then be incorporated in the film.

Nitride films with varying carbon content can be deposited from trimethylsilane and a nitrogen precursor. Table 4 compares the deposition conditions and properties of nitride films grown at 250 °C. In this case the trimethylsilane was used as a one for one substitute for silane in an existing plasma nitride process developed at Dow Corning [3]. Under these conditions flow it is found that the process using (CH₃)₃SiH ("TM-nitride") has approximately one half the growth rate compared to the silane based process ("Si-Nitride"). Figure 2 compares the FTIR spectra of the nitride films from the processes in Table 4. The spectra are very comparable in the 1200-500 cm⁻¹ region. With regards to hydrogen bonding, the TM-nitride process incorporates some C-H bonding in place of N-H in the film. The addition of carbon bonding correlates with the film stress becoming increasingly compressive. Stress-temperature measurements show that the nitride film deposited using the TM-nitride process has a coefficient of expansion which is higher than silicon, whereas the standard nitride film typically has a coefficient of expansion which is lower than silicon. An interesting finding on the TM-nitride process is that wet chemical etching of blanket films in HF solutions was not successful. Standard silane based nitrides have a measurable etch rate in HF.

To explore higher growth rates, the process was adjusted so that flow of the silicon precursor was increased to 18 sccm, He to 162 sccm, and the nitrogen source to 720 sccm at 4200 mT, 360 °C and 250 W. The Si-nitride deposition rate increased to 880 Å/min with 720 MPa of tensile stress, while the TM-nitride process growth rate increased to only 150 Å/min with 200 MPa of tensile stress. FTIR analysis shows a smaller N-H/C-H ratio in the TM-nitride film, which may indicate less nitrogen incorporation than the process listed in Table 4. The Si-nitride blanket films exhibited a 10:1 BOE etch rate of 1300 Å/min, whereas blanket TM-nitrides exhibited no etch rate. The high stress and etch rate of the Si-nitride can be attributed to lack of He dilution in our system [3]. An interesting

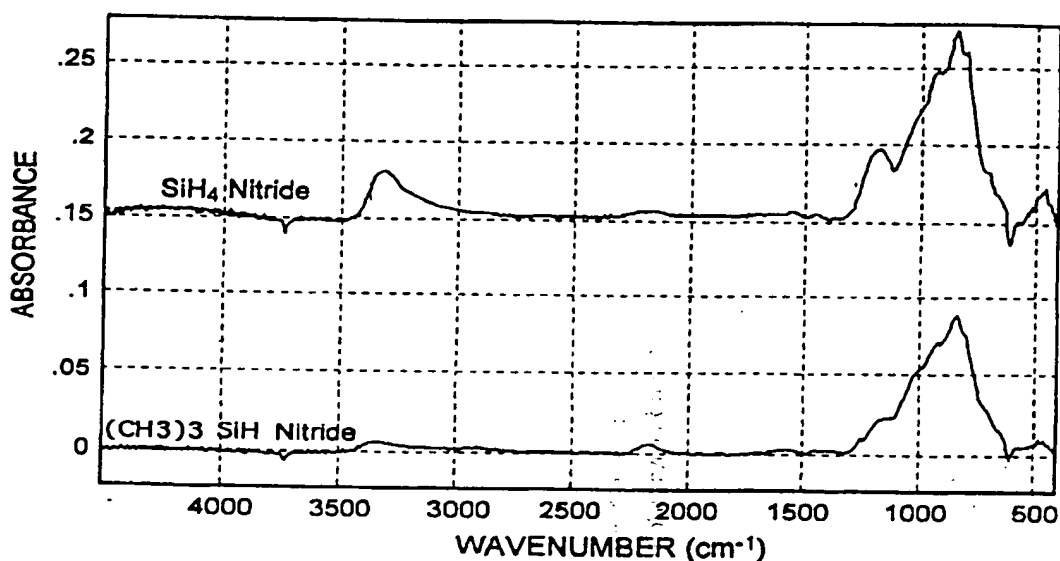


Figure 2. Reflection-absorption infrared spectra of plasma deposited a-SiN:H films deposited using the processes shown in Table 4.

comparison can be seen in the step coverage performance, shown in Figure 3. The Si-nitride shows conformal coverage while the trimethylsilane based nitride exhibits a slight reentrant angle in the side wall coverage. The sidewall density was evaluated by etching for 2.5 minutes in 10:1 BOE. The sidewall of the Si-nitride is severely etched. The sidewall of the TM-nitride shows that a small etch path has formed through the reentrant seam defect. Penetration to the Al-step occurred at the end of the seam where the thickness of the film was at a minimum. There is a slower etch rate in the TM-nitride sidewall, but the process needs to be adjusted to correct the reentrant angle step coverage.

Trimethylsilane has been successfully used to deposit films of amorphous

Table 4 - Example comparison of PECVD Nitride Films Grown at 250° C

	SiH ₄ Process	(CH ₃) ₃ SiH Process
SiH ₄ Flow (sccm)	6	0
(CH ₃) ₃ SiH Flow (sccm)	0	6
10% NH ₃ / 90% N ₂ Flow (sccm)	300	300
He Flow (sccm)	654	654
Pressure (torr)	1.5	1.5
Power (W)	100	100
Growth Rate (Å/min)	239	105
Compressive Film Stress (MPa)	61	196
Composition	Si _{0.31} N _{0.46} H _{0.23}	Si _{0.26} N _{0.33} C _{0.10} H _{0.31}
RBS Density (atoms/cc)	8.8x10 ²²	8.4x10 ²²

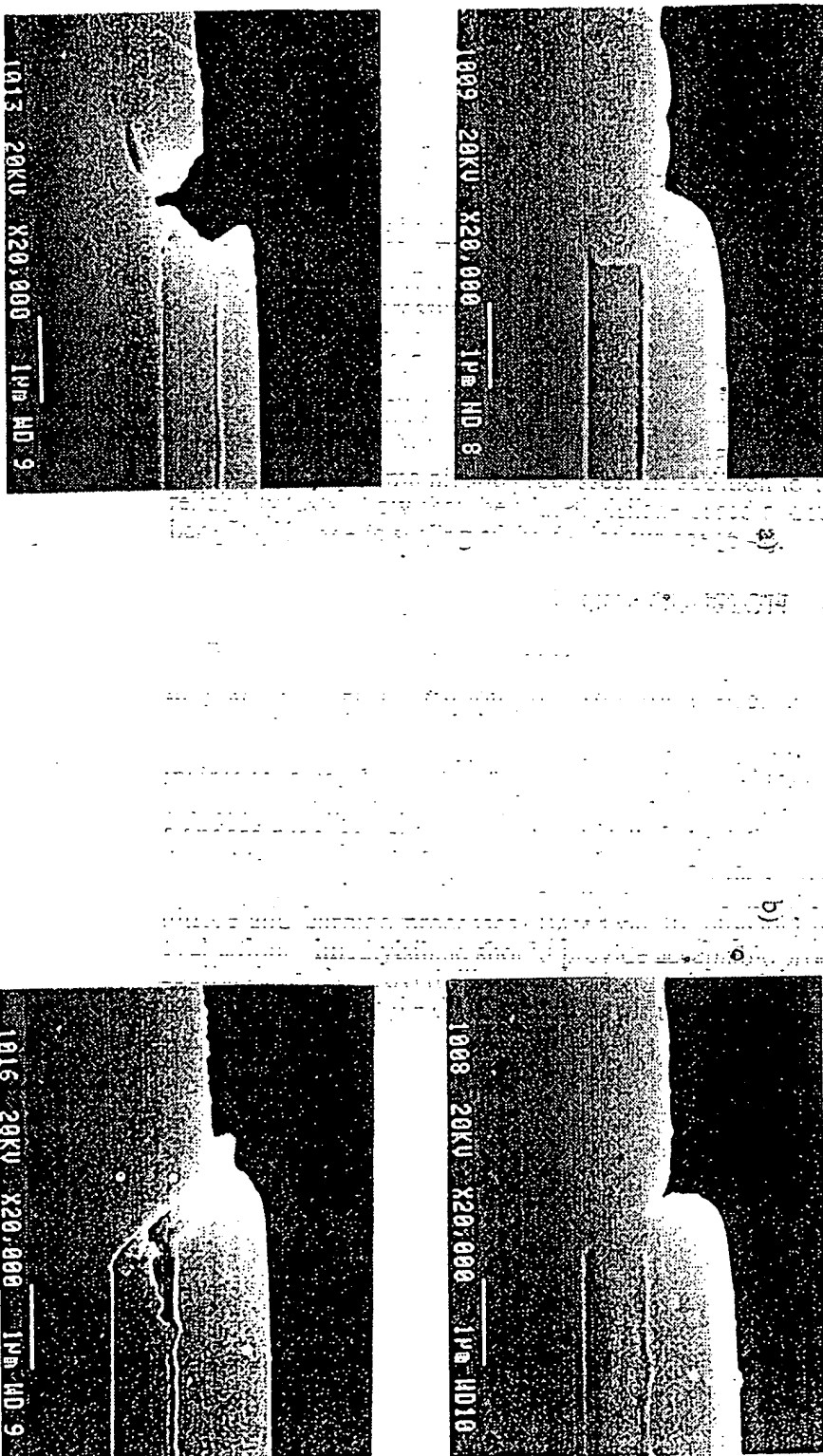


Figure 3. Step coverage of plasma deposited silicon nitride films using a) SiH_4 and b) trimethylsilane. The top figure shows the as deposited film, and the bottom shows the film etch characteristic following a 150 second etch in 10:1 BOE.

hydrogenated silicon carbide (a-SiC:H). Films of a-SiC:H are hard and resistant to chemical attack and moisture [6], making them useful for the protection of integrated circuits [7,8]. Traditional methods use silane and hydrocarbon gases to deposit a-SiC:H films. These processes rely on Si-C bond formation to occur on the growth surface. For thin film protection applications it is desirable that $C/Si > 1$. Silicon rich films have been shown to have higher stress and high dielectric constants [9], characteristics which are undesirable for IC passivation. In order to achieve carbon rich films with an SiH_4/C_xH_y based process, one often observes low growth rates and homonuclear silicon bonding which can result from the low sticking coefficients associated with hydrocarbon radicals. The Si-C bonds maintained in the trimethylsilane radicals increase Si-C bonding in the carbide film [9]. Ratios of C/Si in the range of 1-1.2 are commonly found under standard process conditions. This helps to improve the desirable characteristics such as chemical resistance and film hardness. a-SiC:H films deposited from trimethylsilane do not show reactivity in HF-based oxide and nitride etchants.

Typical PECVD processes for a-SiC:H uses a mixture of trimethylsilane and an inert gas such as Ar or He. Figure 4 plots a-SiC:H film growth, refractive index and stress data for depositions at 2.7 and 4.0 torr. The rate of change of film growth with time is very similar over this pressure range. The data also shows that changing the pressure is one way to manipulate the film stress. Step coverage of the a-SiC:H processes is shown in Figures 5 for the 2.7 torr and 4.0 torr a-SiC:H process. There is no reentrant angle as observed in the TM-nitride process. Also no sidewall etching is observed in the BOE etchant. Similar step coverage was observed with the 4.0 torr process. These properties allow the process to be tailored for improving IC passivation in applications currently addressed by plasma nitride processes. In addition to the chemically-resistant sidewall, reliability tests show that the trimethylsilane based a-SiC:H process offers the additional benefit of hermetic sealing of the device surface [6-8].

CONCLUSION

Examples have been provided to demonstrate the utility of trimethylsilane, $(CH_3)_3SiH$, in plasma based deposition processes for dielectric films used in the fabrication of semiconductor integrated circuits. The properties of the gas itself offer improvements in safety and process reliability, which can help to realize longer durations between maintenance and repair of process equipment. The versatility of this material is demonstrated by its use in a wide range of processes for oxides, nitrides and carbides. In standard process equipment, trimethylsilane based processes will exhibit slightly lower deposition rates under equivalent conditions to silane based processes. Evaluation of step coverage experiments shows that improvements in sidewall density can be obtained in nitride and carbide processes. Based on its physical properties and our experimental evaluation, trimethylsilane should provide acceptable process efficiency in manufacturing applications. Improved film properties such as low stress and hermeticity can be incorporated within the dielectric processes used in IC manufacturing.

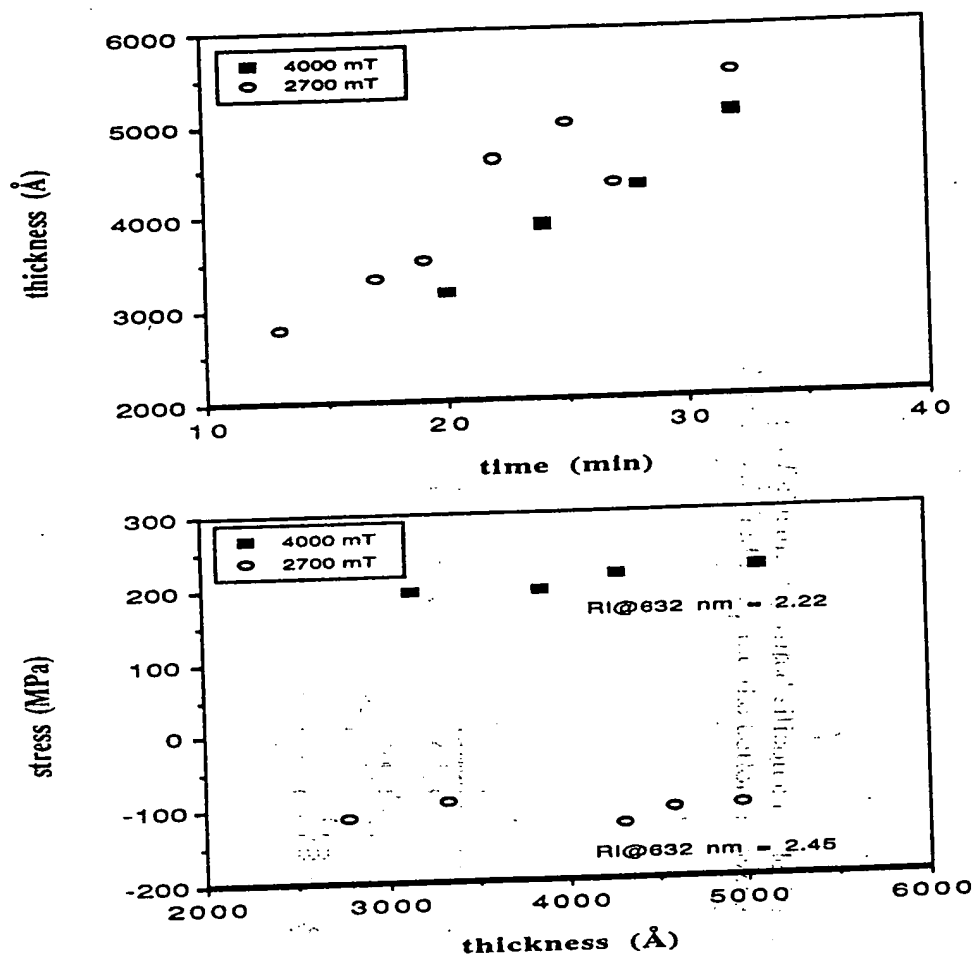


Figure 4. a-SiC:H film growth, stress and refractive index for films grown at 2.7 and 4.0 torr. The process parameters were trimethylsilane flow=100 sccm, He flow=500 sccm, power=350 W, wafer temperature~360 °C.

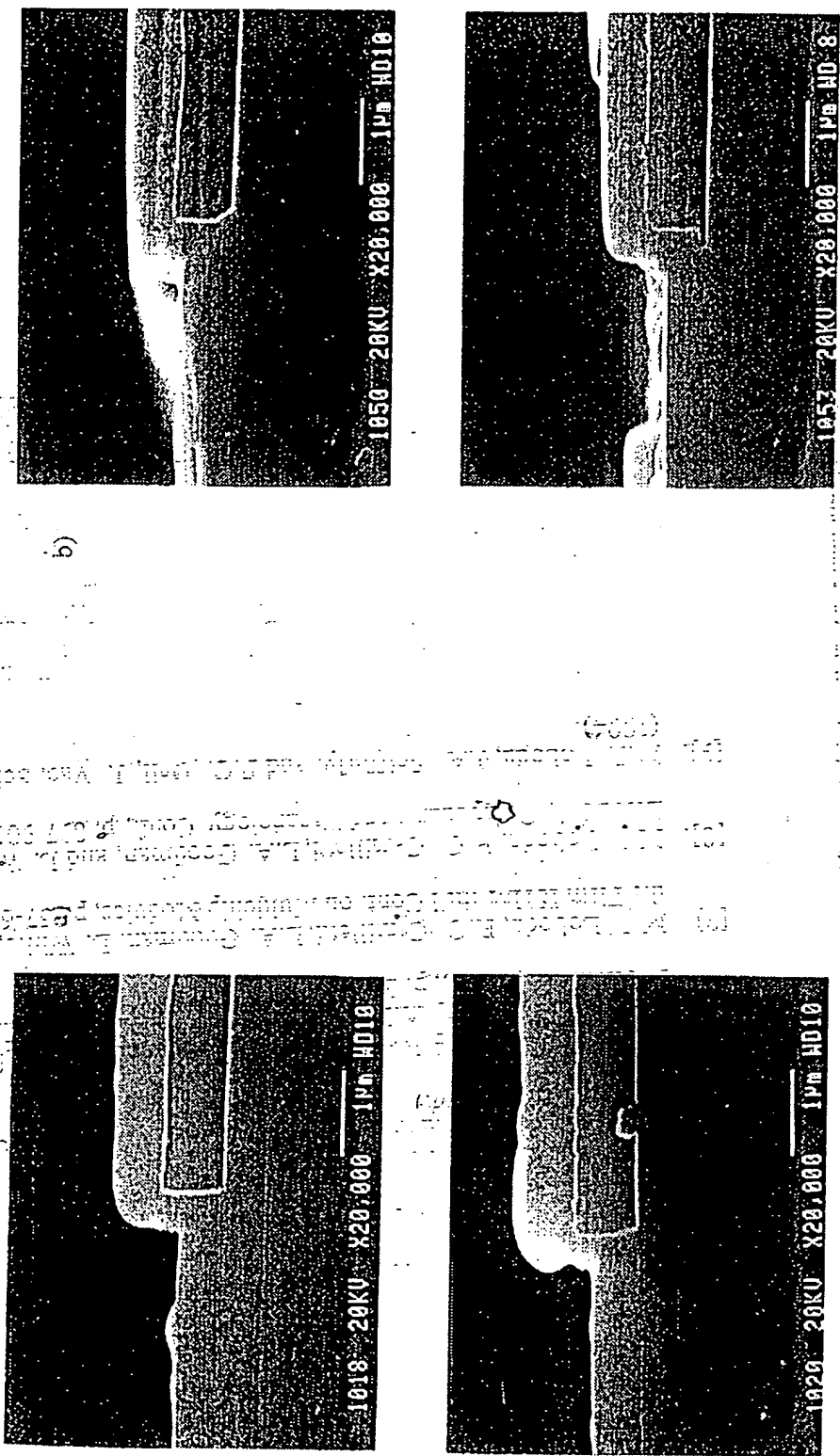


Figure 5. Step coverage of plasma deposited silicon carbide films using trimethylsilane at a) 2.7 torr and b) 4.0 torr. The top figure shows the as deposited film, and the bottom shows the film etch characteristic following a 150 second etch in 10:1 BOE.

- [1].
- [2].
- [3].
- [4].
- [5].
- [6].
- [7].
- [8].
- [9].

REFERENCES

- [1]. SEMATECH Technology Transfer Report #94062405A-ENG, Silane Safety Improvement Project S71
- [2]. L.G. Britton and P. Taylor, Semiconductor Int'l, April 1991, p. 88-92
- [3]. M.J. Loboda and J.A. Seifferly, J. Mater. Res. **11**(2), 391 (1995)
- [4]. R. Walsh, Acc. Chem. Res., **14**, 246 (1981)
- [5]. M.J. Loboda, J.A. Seifferly, C.M. Grove and R.F. Schneider in Environmental Safety and Health Issues in IC Production, (Mater. Res. Soc.Proc., Pittsburgh, PA, 1997 to be published.)
- [6]. M.J. Loboda, in Advances in Coatings Technologies for Corrosion and Wear Resistant Coatings, A.R. Srivatsa, C.R. Clayton, J.K. Hirvonen, eds. (TMS Publications, 1995), p. 281-90
- [7]. M.J. Loboda, R.C. Camilletti, L.A. Goodman, L. White, and G. Adema, Proc. of the Fifth ISHM Int'l Conf. on Multichip Modules, p.257-62, (1996)
- [8]. M.J. Loboda, R.C. Camilletti, L.A. Goodman, and L. White, Proc. of 46th IEEE Electronic Components and Technology Conf., p. 897-901 (1996)
- [9]. M.J. Loboda, J.A. Seifferly, and F.C. Dall, J. Vac. Sci. Technol. A, **12**(1), 90 (1994)